

Fig. 6.4. Relative cost and specific impulse of rocket propellants. Note that the better the performance of the propellant, the higher the cost. LOX, liquid oxygen;  $N_2H_4$ , hydrazine;  $B_2H_6$ , boroethane (diborane);  $OF_2$ , oxygen difluoride; RP-1, kerosene hydrocarbon fuel; JP-1, jet fuel. [*Chem. Eng. News*, 41 (39) 70 (1963) (modified 1975, 1982).]

**SOLID PROPELLANTS.<sup>8</sup>** Solid propellants have advantages over liquids in that they are simple in design and more easily stored, handled, and serviced. They cost less and, because the ingredients are combined in a mold which serves to confine the materials and impart the desired grain configuration, they can be launched expeditiously, and predicted burning rates can be achieved. Originally, solids were classified into two groups: *heterogeneous*, or *composite* propellants (oxidizer and reducer present in two distinct phases) and, *homogeneous*, or *double based* (oxidizer and reducer present in a single or colloidal phase, e.g., nitrocellulose dissolved in nitroglycerin). Small percentages of additives are used to control the physical and chemical properties of the solid propellant. The properties of solid propellants are shown in Table 6.6.

Solid propellants have a variety of applications: as propulsion units for missiles, target drones, and supersonic sleds. Rockets used for the separation of stages during flight and for settling ullage in the liquid-propellant tanks are usually of the solid type; for example, some details of the Minute Man ICBM solid-propellant rocket stages are available.<sup>9</sup> Glass-filament wound casing for both the first and second stages of the submarine-launched Polaris carry a powerful solid propellant. The retro-rockets the Mercury capsule used for atmospheric reentry employed solids. Flowcharts and equipment have not been released, but processing methods have been described.

Artificial satellites are another type of spacecraft that require rocket propulsion for launch-

<sup>8</sup>Sutton, *Rocket Propulsion Elements*, 3d ed., Wiley, New York, 1963; Kit, op. cit.; Solid Groundwork for Solid Rockets, *Fortune* 71, 114(March 1965)(excellent illustrations of case and nozzle fabrication for "modern and fierce compounds that strain the polymer chemist's newfound art").

<sup>9</sup>McGraw-Hill *Encyclopedia of Science and Technology*, vol. 11, McGraw-Hill, New York 1982, p. 723.

**Table 6.5** Current Propellants

Propellant	Application	Specific Impulse*	Density	Combustion Temperature, °C
O <sub>2</sub> /C <sub>2</sub> H <sub>5</sub> OH (92.5%)	Redstone	287	0.99	3116
O <sub>2</sub> /RP-1	Atlas, Thor, Jupiter, Titan I, Saturn, F-1 engine	301	1.02	3400
O <sub>2</sub> /H <sub>2</sub>	Centaur, Saturn, J-2 engine, M-1 engine	391	0.28	2730
WFNA†/JP-4	Small aircraft engines	268	1.33	2960
IRFNA‡/UDMH	Agena, Able	277	1.25	2955
IRFNA/60% JP-4 + 40% (CH <sub>3</sub> ) <sub>2</sub> N <sub>2</sub> H <sub>2</sub>	Bomarc A	269	1.31	2930
N <sub>2</sub> O <sub>4</sub> /50% N <sub>2</sub> H <sub>4</sub> + 50% (CH <sub>3</sub> ) <sub>2</sub> N <sub>2</sub> H <sub>2</sub>	Titan II, Titan III, Trans, Apollo	288	1.21	3090
N <sub>2</sub> O <sub>4</sub> /(CH <sub>3</sub> ) <sub>2</sub> N <sub>2</sub> H <sub>3</sub>	Gemini	288	1.21	3116
IRFNA/MAF§	Bullpup B	270	1.31	2760
90% H <sub>2</sub> O <sub>2</sub> /JP-4	Small aircraft engines	266	1.29	2525
90% H <sub>2</sub> O <sub>2</sub> monopropellant	Mercury, many others	151	1.39	760
N <sub>2</sub> H <sub>4</sub> monopropellant	Mariner, Ranger	191	1.01	621

\*Pounds of thrust per pound of weight of propellant burned per second. See text.

†WFNA, White fuming nitric acid.

‡IRFNA, Inhibited red fuming nitric acid.

§MAF, Mixed amine fuel.

SOURCE: *Chem. Eng. Prog.* 60 (7) 73 (1964).

**Table 6.6** Solid Propellants for Rockets

Propellant Type	Castable Composite	Extruded Double-Base*
Propellant system	Oxidizer-fuel, NH <sub>3</sub> ClO <sub>4</sub> ·(C <sub>2</sub> H <sub>4</sub> O) <sub>n</sub>	NC, NG, miscellaneous
Typical ingredient variation, %	KClO <sub>4</sub> (50–85), (C <sub>2</sub> H <sub>4</sub> O) <sub>n</sub> (50–15)	NC (50–60), NG (30–45), miscellaneous (1–10)
Adiabatic flame temperature, C°	1540–2480	2100–2900
Typical sea-level specific impulse	175–240	205–230
Characteristic velocity, km/s	1.16–1.46	1.37–1.52
Density, g/cm <sup>3</sup>	1.52–1.74	avg. 1.61
Lower combustion limit, kPa	>1360	
Probable allowable operating-temperature limits, C°	–57 to 112	– 29 to 96
Storage stability	Good	Fair
Smoke	Much at low oxidizer; little at high oxidizer, mist at relative humidity greater than 80%.	Little
Mechanical properties	Soft and resilient to hard and tough	Hard and tough

ing. Several have been placed in the earth's orbit, some for communications (Telstar), for meteorological observations (Zeros), for scientific measurement, for human space flight, and to detect nuclear explosions.

### **MISCELLANEOUS INDUSTRIAL EXPLOSIVE USES**

There are a number of industrial procedures which make use of small quantities of explosives which are highly important. Explosive rivets can be placed without backing devices. Explosive thrustors, pin pullers, separators, and release devices were extremely reliable on the space missions and find use in industrial emergency devices. Forming, shaping, and cladding metals by explosive welding have become important manufacturing techniques. Explosive welding is used to form plate heat exchangers. Shearing and punching of metals works very well. Ejection seats are explosive powered. Electrical cable and connectors are now being attached by firing explosive charges. Metal powders are compacted into formed shapes by use of explosives. Wherever a directed, reliable, swift blow can accomplish a task, an explosive may well be the preferred choice. Much remains to be discovered.

### **PYROTECHNICS**

Because of antifireworks laws, the pyrotechnics industry has now only a fraction of its former importance. Pyrotechnic mixtures, however, still have a number of uses: illuminating flares, marine signal rockets, the red signal flare (fusee) used by trucks and trains for signaling an emergency, and colored light mixtures used for military purposes. In general, these products consist of mixtures of strong oxidizing agents, easily oxidizable materials, and various other materials which act as binders and which alter the character of the flame, together with the color-producing chemical itself. A typical composition used in the manufacture of illuminating flares contains the following materials: barium nitrate (oxidizing agent), 34%; magnesium (to give heat), 36%; aluminum powder (to give strong light), 8%; sodium oxalate (to give a yellow tint), 20%; and calcium stearate, castor oil, and linseed oil (as binders), 2%. As this formula does not fire readily, an igniter consisting of a mixture of 75% black powder and 25% of the above formula is always used to start the flame. A mechanical device starts the combustion of the formula.

### **MATCHES**

The manufacture of matches is an essential industry that is highly mechanized. At present, practically all matches fall within two categories, safety matches and strike-anywhere matches. The match head composition of the latter consists essentially of a fuel with a low kindling point, usually phosphorus sesquisulfide ( $P_4S_3$ ), an oxidizing agent such as potassium or barium chlorate, ground glass, and glue. Safety matches are ignited by the generation of heat on the striking surface of the box, the coating of which consists mainly of red phosphorus, ground glass, and glue. No phosphorus sesquisulfide is used in safety matches, but antimony sulfide is used in the heads as a flame-producing agent.

## MILITARY EXPLOSIVES

Cost is less vital in the case of military explosives and the accent is on performance and good storage life. More organic materials are used than in industrial work, but ammonium nitrate remains the major explosive substance.

A complete round of ammunition is everything necessary to fire a shot. Military ammunition varies in size from caliber 30 (0.30 in = 7.6 mm bullet diameter) to 17 in = 432 mm weapons. The essential ingredients for a complete round of high-explosive ammunition is shown in Fig. 6.5.

The unit consists of a thin cartridge case holding the primer, igniter, and propellant charge. The case is designed to fit smoothly into the gun and, on explosion, to expand, sealing the breech of the gun so that the escape of gases to the rear is prevented, thus allowing the full effect of the propellant to be exerted on the projectile half of the shell. The primer contains a small amount of a priming mixture [e.g.,  $\text{KClO}_3 + \text{Pb}(\text{CNS})_2 + \text{Sb}_2\text{S}_3 + \text{TNT} + \text{ground glass}$ ]. This mixture explodes under the impact of the firing pin and produces a flame which ignites the black powder charge of the igniter which in turn ignites the propellant charge of coarse-grained smokeless powder. The burning of the smokeless powder causes the rapid emission of heated gas, which ejects the projectile from the gun. At the target, upon impact or upon functioning of the time-fuze mechanism, a small quantity of a primary explosive (the detonator) is set off; this causes explosion of the booster—an explosive of intermediate sensitivity (between that of a primary explosive and the bursting charge)—which picks up the explosive shock from the detonator, amplifies it, and ensures complete detonation of the bursting charge. The bursting charge of high explosive is usually TNT alone or mixed with ammonium nitrate. Most bursting charges are mixtures, for example amatol ( $\text{TNT} + \text{NH}_4\text{NO}_3$ ), compound B ( $\text{RDX} + \text{TNT}$ ), pentolite ( $\text{PETN} + \text{TNT}$ ), tetratol (tetryl + TNT), and octol (aluminum + TNT +  $\text{NH}_4\text{NO}_3$ ). Ammonium picrate is used for armor-piercing shells because of its extraordinary resistance to shock. Industrial and military explosives both use the same chain initiator—primer (blasting cap), booster (booster), bursting charge (blasting agent) pattern, except for the fuze, which is some type of mechanical or electronic device to cause explosion on impact, delayed on impact, or by proximity, as desired.

Many military explosives have at least some industrial use, which is not surprising, since many military and industrial uses are similar. Smokeless powder, black powder, and primers have all been discussed earlier. Military units tend to be larger, the performance demanded requires better quality control, and the effects of really long-time storage under difficult conditions must be minimized. Some major explosives used are listed below.

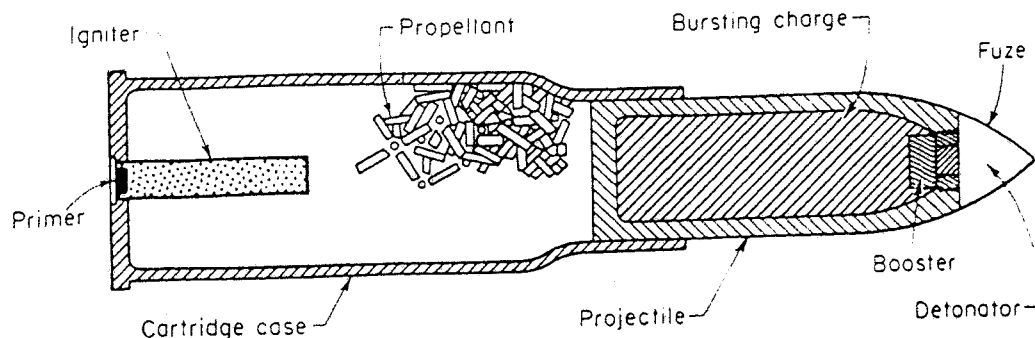


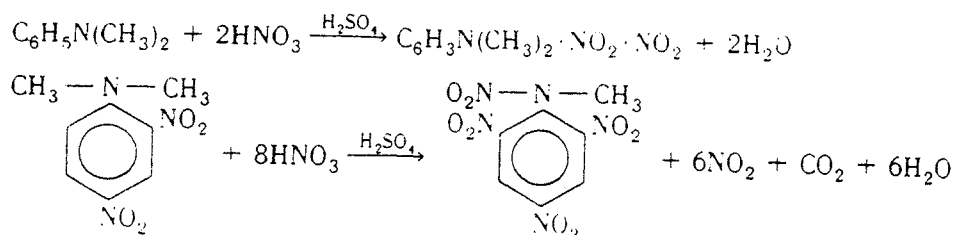
Fig. 6.5. Complete round of high-explosive ammunition.

## TNT (Trinitrotoluene)

In spite of other new explosives developed, symmetrical TNT remains an important military explosive, particularly in mixtures with ammonium nitrate. Its low melting point (80°C) permits loading into bombs and shells in the molten state. It does not have picric acid's tendency to form shock-sensitive metallic salts. TNT is made by multiple-stage nitration of toluene with a mixture of nitric and sulfuric acids. Three-stage nitration to mono-, di-, and trinitrotoluene was formerly used, but continuous-flow stirred-tank reactors and tubular units using the countercurrent flow of strong acids and toluene permit better yields, control, and lower costs.<sup>10</sup>

## Tetryl

Tetryl [2,4,6-trinitrophenylmethylnitramine,  $C_6H_2(NO_2)_3NCH_3NO_2$ ] is chiefly used as a base charge in blasting caps, as the booster explosive in high-explosive shells, and as an ingredient of binary explosives. It is generally prepared by the action of mixed sulfuric and nitric acid on dimethylaniline in a multiple-stage nitration.



It may also be made by alkylating 2,4-dinitrochlorobenzene with methylamine and then nitrating.<sup>11</sup> Tetryl is a powerful high explosive with intermediate sensitivity and great shattering power.

## Picric Acid

Picric acid (2,4,6-trinitrophenol) is not made by the direct nitration of phenol, because too many oxidative by-products are formed. It is manufactured instead by the nitration of mixed phenolsulfonates with mixed acid.<sup>12</sup> Mixed acids cut down the health hazard caused by fuming, reduce the amount of acid required, and increase the yield of desired products. The use of mixed acid is now almost universal. Its heavy-metal salts are dangerously sensitive, and its major use is for the manufacture of ammonium picrate.

## Explosive D

Explosive D, or ammonium picrate, is made by the neutralization of a hot aqueous solution of picric acid with aqueous ammonia.

<sup>10</sup>Albright, Processes for Nitration of Aromatic Hydrocarbons, *Chem. Eng.* 73 (10) 161 (1966); Prime, Seven-Stage Nitration of TNT, *Chem. Eng.* 71 (6) 126 (1964).

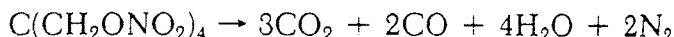
<sup>11</sup>*Military Explosives*, Depts. of the Army and Air Force, Technical Manual TM9-1910, April 1955, p. 157.

<sup>12</sup>Formerly, strong nitric acid alone was used.

It is used in armor-piercing shells as a bursting charge. Because is a salt, it does not melt so it must be loaded by compression.

### **PETN**

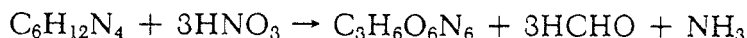
PETN, pentaerythritol tetranitrate  $C(CH_2ONO_2)_4$ , is one of the most brisant and sensitive of the military high explosives. For use as a booster explosive, a bursting charge, or a plastic demolition charge, it is desensitized by admixture with TNT or by the addition of wax. PETN may be made by the nitration of pentaerythritol with strong (96%) nitric acid at about  $50^\circ\text{C}$ . The reaction of decomposition is probably:



PETN is used in making detonating fuses and commercial blasting caps, and has a small medicinal use.

### **RDX**

RDX, cyclonite, or *sym*-trimethylenetrinitramine  $[(CH_2)_3N_3(NO_2)_3]$ , is one of the most powerful explosives known at the present time. RDX is used in a mixture with TNT and aluminum, known as Torpex, for mines, depth charges, and torpedo warheads. It is also employed as an ingredient in explosives for shells and bombs and is desensitized by wax or oily materials. Pentolite, made by casting slurries of PETN with TNT, has specialized uses; for example, 50:50 pentolite is used as a booster for slurry blasting agents and prilled ammonium nitrate-fuel oil mixtures and as the main charge in Procore boosters. The British developed the first practical synthetic process, which involved the destructive nitration of hexamethylenetetramine with concentrated nitric acid:

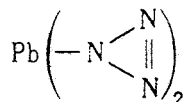


A combination process was developed by Bachman at the University of Michigan, who utilized the by-products to obtain a second mole of RDX. This method was developed on a continuous scale by Tennessee Eastman, which manufactured it the most economically (yields of 70 percent).



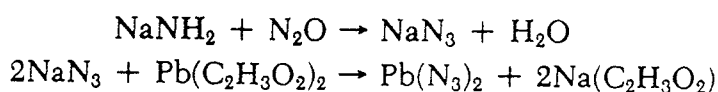
Some by-products of this reaction are also useful as explosives.

### **Lead Azide**



Lead azide has largely replaced mercury fulminate as an initiating explosive for blasting caps. The fulminate has less than desirable stability, has to be manufactured in small batches, and is

involves scarce and poisonous mercury. Lead azide has remarkable stability, involves no strategic materials, and can be manufactured in large batches by treating sodium azide with lead acetate or nitrate. Sodium azide can be made from sodium amide and nitrous oxide.



### ***Lead Styphnate***

Styphnic acid is trinitroresorcinol and forms two salts on reaction with lead acetate or nitrate, basic lead styphnate  $[\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OPbOH}]$ , and lead styphnate. The basic styphnate is a favored primer ingredient. Styphnic acid can be prepared from dinitrochlorobenzene, but nitration of resorcinol gives very poor yields.

## **INCENDIARIES**

Flammable mixtures are probably the oldest chemical weapons known to humans; the destruction of many ancient cities was due to the use of fire. Samson tied firebrands to the tails of foxes and ran them through the Philistine's grain fields. Incendiaries were the largest single category of chemical supplies consumed during World War II and were vital factors in that victory. An incendiary, strictly speaking, causes ignition of combustible materials at the target, e.g., wooden buildings or petroleum products. Incendiaries take the form of bombs, bomblets, artillery shells, and grenades. Incendiaries fall into two classes, metallic and petroleum. Metallic incendiaries provide intense sources of ignition, petroleum units scatter less intense sources widely. Metallic incendiaries include bombs with metallic cases, usually made of a combustible magnesium alloy filled with a mixture of barium nitrate and aluminum with thermite to ignite the case. Thermite is a mixture of aluminum powder and iron oxide which, when ignited, burns fiercely at a high temperature and cannot be extinguished by means of water.



Some readily ignitable material, such as black powder, is employed to ignite the thermite. Sometimes white phosphorus or a small amount of tetryl is added as a deterrent to fire fighters.

Petroleum incendiaries contain gasoline thickened with various ingredients. The first satisfactory thickener was rubber, but other thickeners such as isobutyl methacrylate polymer, which was dissolved in gasoline in combination with calcium soap, were discovered. Perhaps the most important thickener is napalm. This is a granular aluminum soap prepared by precipitating aluminum sulfate in excess alkali with two parts of acids from coconut oil, one part of naphthenic acid, and one part of oleic acid. The soap is capable of withstanding elevated temperatures and produces a gasoline jelly at ordinary temperatures by simple mixing. Napalm surpasses rubber gels in effectiveness and is applicable in flame throwers where rubber gels would be too viscous. It was because of napalm that the flame thrower became such an important and formidable weapon.

Flame weapons provide the fuel for a fire which destroys the target by heat, e.g., personnel, weapons, or electronic equipment. Flame weapons are usually massive bombs or armored, vehicular-mounted flame throwers. Flame weapons also ignite combustible material present at the target. Flame throwers enjoy a limited use for controlling unwanted vegetation.

## **TOXIC CHEMICAL WEAPONS**

Modern use of toxic chemicals in war began in 1915, with the release of a large quantity of chlorine, a gas which was rather ineffective because of its low molecular weight and consequent high diffusion rate which made it difficult to create and maintain casualty-producing concentrations in the areas desired. Contact poisons such as "mustard gas" were more effective. Such agents are persistent because of low vapor pressure. A variety of improved toxic agents have been devised containing both chemical and biological materials. Used against an unprepared enemy, these agents are very effective. Used as a defensive weapon to deny an area to an enemy, these agents might be useful, but as an offensive weapon they require difficult decontamination before advancing troops can enter. Protective clothing and self-contained breathing apparatus hamper movement and greatly reduce effectiveness. Use of toxicants is universally condemned, but mutual fear and distrust keeps interest in their development alive.

Toxic agents designed to produce temporary incapacity are of value in controlling riots and civil disobedience. Such materials may produce sneezing, tears, vomiting, and/or nausea. Gas masks are rarely effective and self-contained breathing apparatus is required for adequate protection. Common tear gases include chloroacetophenone, brombenzylcyanide, and *o*-chlorobenzylmalonitrile.

## **SCREENING SMOKES**

Smokes or persistent fogs are used to hide areas on a temporary basis. Smokes are dispersed by mechanical, thermal, and chemical means. Most fogs are created by forming low volatile droplets of water which remain dispersed in air. White phosphorus, which burns to  $P_2O_5$ ; hexachloroethane-zinc combustion, which forms  $ZnCl_2$ ; and sulfur trioxide, and chlorosulfonic acid, which gives off  $HCl$  and  $H_2SO_4$ , are used to create chemical nuclei for fog formation. Oil vapor mists are used in smoke grenades. Colored smokes are made by burning pyrotechnic mixtures which volatilize various heat-resistant organic dyes.

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## Chapter 7

# Photographic Products Industries

The word "photography" is derived from two Greek words which mean "drawing by light." Vision is the most common method humans have at their disposal for receiving and conveying impressions of the world in which they exist—ample proof of the importance of photography to modern civilization. There is no field of human activity at the present time, whether it be industry, science, recreation, news reporting, printing, or the mere recording of family histories, which is not, in some phase or other, touched upon by the photographic process. Although it is one of the youngest of the chemical process industries, it has universal appeal.

**HISTORICAL.<sup>1</sup>** The first recorded use of a lens for image formation occurred in the latter part of the sixteenth century. The effect of light on silver salts was known to the early alchemists, but it was Wedgwood, son of an English potter, who at the beginning of the nineteenth century first successfully reproduced images as negatives on paper impregnated with silver salts. In 1819, Herschel discovered the fixing properties of *sodium thiosulfate*, thus paving the way for permanent pictorial reproductions and making possible the first exhibit, in 1839, of so-called "photographs." The same year, a Frenchman, Daguerre, released to the public his formula for the manufacture of the familiar daguerreotype, and an American, Draper, made what was probably the first photographic portrait.

The announcement of these processes created a demand for better lenses, which was soon satisfied. In 1851, Archer improved and perfected the "wet-collodion" process, but in the hands of the public all the collodion processes eventually bowed to the superior gelatin dry plate discovered by Maddox. Vogel at the University of Berlin in 1873 discovered that dye molecules adsorbed on the silver halide crystals greatly increased the light sensitivity of these crystals (spectral sensitization). In 1889, George Eastman introduced transparent roll film and popularized the now familiar snapshot camera. Soon after this, practical methods for producing motion pictures were invented. Color-sensitized emulsions were used as early as 1904 by the Hoechst Dye Works of Germany, and the famous Wratten panchromatic plates were introduced in 1906. Velox developing paper was announced in America at about the same time, as the result of the discoveries of Leo H. Baekeland. Portrait film was introduced about 1920, and projection printing came into general use about the same time. Since the early 1920s, developments in all phases of the art have been fundamental and rapid, culminating in the introduction of natural color film about 1928 and practical amateur color prints in 1941. It is this latter field, color photography, that now holds the most promise for the future. The present advanced position of the photographic industry was attained as a result of thorough research on the fundamentals in this field and their application.

<sup>1</sup>ECT, 3d ed., vol. 17, pp. 611-656, 1982.

**USES AND ECONOMICS.** Photography finds widespread application. The amateur uses it in three major ways, for prints (both "instant" and from color negatives), home movies, and small transparencies. Professional usage is more varied: entertainment, education, sales promotion, graphic reproduction in magazines, display advertising, industrial illustration, data recording, nondestructive testing including photography, and medical and scientific records. In the United States 14 percent of the products are purchased for medical use, 13 percent by professional movie makers, 14 percent for photocopying and reproduction, 25 percent by business and commercial users, and 36 percent by amateurs. It is estimated that yearly more than  $6 \times 10^9$  still pictures—about 85 percent in color—are made by amateurs. In home movies, color film has almost completely (99 percent) displaced black-and-white

## PHOTOGRAPHIC PROCESS

Photography is the process of producing a visible image upon a substance by the action of light or other radiant energy. Thus ultraviolet and infrared are included as initiators, and the word "light" encompasses that portion of the electromagnetic spectrum from the ultraviolet region through the visible region and into the infrared. In the case of the economically significant photographic processes, the "light" sensitive substances employed are silver halides, diazo compounds, amorphous selenium, organic photoconductors, and zinc oxide. Silverless films are widely used for medical x-rays, graphic arts, and engineering drawings. They have not taken over the consumer market because they are *slow* compared with silver halide film.

A new development that threatens to take over some of the silver film market is the introduction of an electronic camera which uses videotape instead of film to produce the image.

Silver halides are employed as the sensitive substance in the most widely used photographic materials.<sup>2</sup> Such materials have a natural sensitivity to ultraviolet and blue radiation. Their sensitivity to green, red, and infrared is negligible unless special sensitization to these regions is induced by adsorption of so-called sensitizing dyes on their surfaces. Sensitization to blue, green, and red is particularly important in the representation of colors as shades of gray in black-and-white photography and in their simulation in color photography. Light-sensitive silver salts are prepared in the dark as aqueous gelatin "emulsions" which, after proper additional treatments, are coated on a support which may be glass, paper, plastic, or some other material. Although manufacturers closely guard exact procedures employed in preparing commercial emulsions, the general principles are described in the literature.<sup>3</sup> The technology is complicated, and the user of photographic materials generally purchases a packaged coated product.

Exposure of the emulsion in a camera or other suitable device results in a photochemical reaction on the surface of the silver salt crystal. Photolytic silver, constituting a *latent image*, forms roughly in proportion to the amount of incident light of the color to which the crystal is sensitive. The latent image serves to catalyze further conversion of the entire crystal to a

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<sup>2</sup>The photographic industry used 1650 t ( $53 \times 10^6$  troy ounces) of silver in 1981; *Chem. Week* 130 (26) 13 (1982).

<sup>3</sup>Sturge, (ed.), *Neblette's Handbook of Photography and Reprography*, 7th ed., Van Nostrand Reinhold, New York, 1977; Duffin, *Photographic Emulsion Chemistry*, Focal, London, 1966.

metallic silver image upon the action of a developing agent. The density of the image depends upon the number of crystals exposed and the extent to which development is permitted to occur. Crystals which did not become exposed or were insensitive to the exposing light develop slowly or not at all. Removal of these silver salts and the undeveloped portions of those which had been exposed is accomplished by the formation of soluble complexes, which are later washed from the material by water. The result of this process is an image whose density bears a direct relationship to the intensity of the initiating light energy. Thus a light object is reproduced as a dark image, and vice versa. When the sensitive material is exposed in a camera, the result of the process described above is a negative. Positives, or prints, are generally produced by using the negative to modulate the exposure of a second piece of photographic material, followed by processing as above.

Recent technological advances have brought direct-positive or reversal camera films to the market. Direct-positive photographic images are obtained by first developing the negative silver image and then dissolving the silver in an oxidizing solution or "bleach." The residual complement of silver halide, which has the configuration of the positive image, is uniformly fogged either physically by light or chemically by a reducing agent and then developed to give a positive silver image.

**PHOTOGRAPHIC EQUIPMENT AND MATERIALS.** All films and plates consist essentially of an emulsion on a film support of cellulose acetate, polyester, or glass. The *emulsion* is composed of a suspension of minute silver halide crystals in gelatin, suitably sensitized by the addition of certain dyes or various classes of sulfur and gold compounds. In addition, antifogging agents, hardening agents, stabilizers, coating aids, and an antihalation backing are used. Halation is fogging of the emulsion by light reflected into it from the back surface of the film. The back of the film is generally coated with a layer of hardened gelatin to prevent curling. Table 7.1 lists important photoprocessing chemicals and their functions.

**PROCESSING OF BLACK-AND-WHITE MATERIALS.** Modern developing solutions contain mainly four functional constituents: an organic reducing agent, a preservative, an accelerator, and a restrainer. The function of the *reducing agent* is to chemically reduce the silver halide to metallic silver at the various points where light has produced the latent image. As this reduction is a rate process, practical *developers* are those which reduce silver halide in contact with a latent image to silver much faster than they reduce the silver halide unaffected by light. Chemically, they are polyhydroxide, amino hydroxide, or polyamine derivatives, and are mostly aromatic. The developing agents which are commercially important are hydroquinone, *p*-methylaminophenol (Elon, Metol), certain heterocyclic substances such as Phenidone, and *p*-phenylenediamines. The last mentioned are particularly important in color photography and will be discussed further. *Preservatives* guard the developer against air oxidation. The most common is sodium sulfite, but the bisulfite and metabisulfite are also employed. *Accelerators* increase the alkalinity of the developing solution, hence increase the activity of most of the developing or reducing agents. They include the carbonates of sodium and potassium, sodium metaborate, and borax. Antipollution laws in several states have caused the use of borates and borax to be discontinued. In order to control the speed of the developer, it is necessary to employ a *restrainer*, usually potassium bromide or a heterocyclic compound such as benzotriazole.

The theory of the development of the photographic image is connected with the properties of the emulsion. In the silver halide crystals internal dislocations act as electron traps. When a minute amount of light energy is absorbed by the silver halide, a free atom of silver is

**Table 7.1** Selected Photoprocessing Chemicals Used in Black-and-White Photographs  
(Chemicals Represent Approximately 2% of Processing Costs)

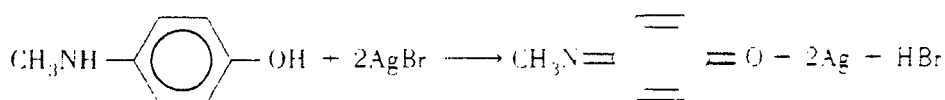
Use	Common or Trade Name	Chemical Name	Action
<b>Developing agents</b>			
Capable of reducing exposed crystals of silver halide in emulsion to silver without reducing unexposed crystals at the same time	Hydroquinone Metol, Elon Phenylenediamine Phenidone	<i>p</i> -Dihydroxybenzene <i>p</i> -Methylaminophenol <i>p</i> -Phenylenediamine 1-Phenyl-3-pyrazolidone	Slow, powerful Fast True grain (toxic) Forms superadditive mixtures with other developing agents
<b>Activators</b>			
Activate developing agent and control pH		Sodium carbonate Potassium carbonate	Controls pH Controls pH
<b>Preservatives</b>			
Guard against oxidation Prevent staining of emulsion		Sodium sulfite Sodium carbonate Sodium citrate	Transforms oxidation products into colorless compounds
<b>Restrainers</b>			
Prevent chemical fog		Potassium bromide 6-Nitrobenzimidazole Benzotriazole	Lowers degree of ionization of silver bromide
<b>Calcium precipitants</b>			
Prevent sludging	Calgon Quadrafos	Sodium hexametaphosphate Sodium tetraphosphate	Forms complex compounds Forms complex compounds
<b>Wetting agents</b>			
Facilitate absorption of developing solution	Denatured alcohol	Ethyl alcohol	
<b>Neutralizer</b>		Acetic acid	Stops development by acidification
<b>Fixatives</b>			
Dissolve unexposed silver halides	Hypo	Ammonium thiosulfate Sodium thiosulfate	Converts silver halides into water-soluble compounds
<b>Hardeners</b>			
	Aluminum, chromium, and ferric salts Organic aldehydes	Chrome alum Glyoxal, formaldehyde	Hardens gelatin to insolubilize it and increase mechanical strength
<b>Intensifiers</b>			
Increase density	Chromium compounds Silver compounds + hypo	Potassium dichromate	

**Table 7.1** (continued)

Use	Common or Trade Name	Chemical Name	Action
Reducers			
Reduce density	Potassium ferrocyanide with hypo		Varies with concentration
	Potassium permanganate and sulfuric acid		oxidation of silver

SOURCE Augmented from Glafkides, *Photographic Chemistry*, Fountain, London, 1958; modified by 1975 SPSE *Handbook of Photographic Science and Engineering*, Wiley, New York, 1975.

liberated. This silver atom acts as a center which attracts more photolytically generated silver atoms until a positively charged stable latent image site capable of being developed,  $\text{Ag}_2^+$ , is formed. This latent image is changed into a visible image by the developer's depositing sufficient metallic silver from the silver halides of the emulsion on these nuclei. In the presence of sufficient sulfite, a typical developer, *N*-methyl-*p*-aminophenol (Metol) probably reacts as follows:



Development is arrested at the desired point by immersing the photographic material in a mildly acid bath, usually dilute acetic acid, which destroys the alkaline condition necessary for development.

Modern *fixing agents* are of a nonhardening or acid-hardening type. Their main purpose is to render the silver image permanent by dissolving away the undeveloped silver halide. The type most commonly employed includes a silver halide solvent (sodium or ammonium thiosulfate), an antistaining agent (acetic or citric acid), a preservative (sodium sulfite), and a hardening agent (potassium chrome alum or formaldehyde).

The processing of black-and-white photographic materials is concluded by a *wash* in running water to remove the silver halides solubilized by the fixing baths. Thorough washing is necessary for long-term stability of the image to avoid staining and bleaching due to decomposition of unremoved silver complexes. After washing, the materials are dried, often with heat. Where long-term stability or highest quality is not necessary, or where rapid access to the final image is desired, stabilization processing is sometimes employed. This process often consists of two baths: a conventional developer, followed by the stabilizing bath itself, which often contains sodium thiosulfate, potassium thiocyanate, or urea. The silver complexes thus formed are not washed from the material.

The photographic process may be summarized by these steps: exposure of the negative film or plate in a camera, followed by development of the latent image, fixing of the image by removal of the unaffected but still sensitive silver halides, and drying of the negative. The negative is used to make a positive, usually on paper, which is subjected to the same sequences of exposure, development, fixation, and drying.

The recovery of silver from used processing solutions is important both from economic considerations and because of environmental concerns. Silver is also recovered from discarded negatives and prints and scrap film.

Several methods for silver recovery are described in great detail in the patent literature. The common methods are electrolytic plating out of the silver from the spent solutions using a stainless-steel cathode or by the immersion of two dissimilar metals in the solution. The silver in solution can also be precipitated as free silver from solution by reduction with steel wool, zinc dust, or hydrosulfites and by treatment with sulfides to precipitate silver sulfide.

Reverse osmosis is one of the more recent methods of removing silver salts from solution. The silver halides can be extracted with an acidified water-nitrile mixed solvent, and the solvent solution subjected to reverse osmosis through a suitable membrane to concentrate the silver salts.

## **COLOR PHOTOGRAPHY—THEORIES, MATERIALS, AND PROCESSES**

Color photography<sup>4</sup> is based upon the principle that the colors of nature can be adequately represented to the eye and brain by mixtures of blue, green, and red light. Such mixtures have been produced by projecting in register colored beams of light emanating from properly prepared transparent positive images or by modulating, by silver images, microscopic blue, green, and red filters which are juxtaposed on a support. In the latter method, the eye receives from any area of the picture the amounts of blue, green, and red necessary to reproduce the intended color in that area. A color television picture tube is an electronic analog of this system.

The use of blue, green, and red beams or filters is difficult in practice and is wasteful of light energy. Most methods of color photography are based on the *complements* of blue, green, and red, which are yellow, magenta, and cyan, respectively. Yellow results when blue is absent from white light; magenta, when green is absent; and cyan, when red is absent. Thus a yellow filter controls the blue component of white light while permitting green and red to pass; magenta controls green while permitting blue and red to pass; and cyan controls red while permitting blue and green to pass. Therefore combinations of various densities of yellow and magenta produce a variety of colors, including orange and red; yellow and cyan produce greens; and magenta and cyan produce blues. These combinations can be effected by superimposed dye-containing layers on a single support.

Originally color prints were prepared by applying layer upon layer of pigment to a single print. This process has become almost obsolete with the advent of the much more convenient dye-transfer system. However, there is still some interest in the pigment process because prints thus produced have much more permanent colors than those produced with dyes.<sup>5</sup>

The upper cross section in Fig. 7.1 shows the arrangement of blue-, green-, and red-sensitive emulsion layers and the effect of exposure. A yellow filter layer prevents blue light from reaching the green- and red-sensitive layers, which retain sensitivity to blue. The dyes are located as shown in the other sketches, depending on the color-product objective. Dyes with properties suitable for color photography are produced when the development is accomplished by *p*-phenylenediamines in the presence of an active species called a *coupler*. The

<sup>4</sup>Thirtle, Inside Color Photography, *CHEMTECH* 9 (1) 25 (1979); ECT, 3d ed., vol. 6, 1979, pp. 617-682.

<sup>5</sup>Wall Street Journal, July 1 1981, p. 48.

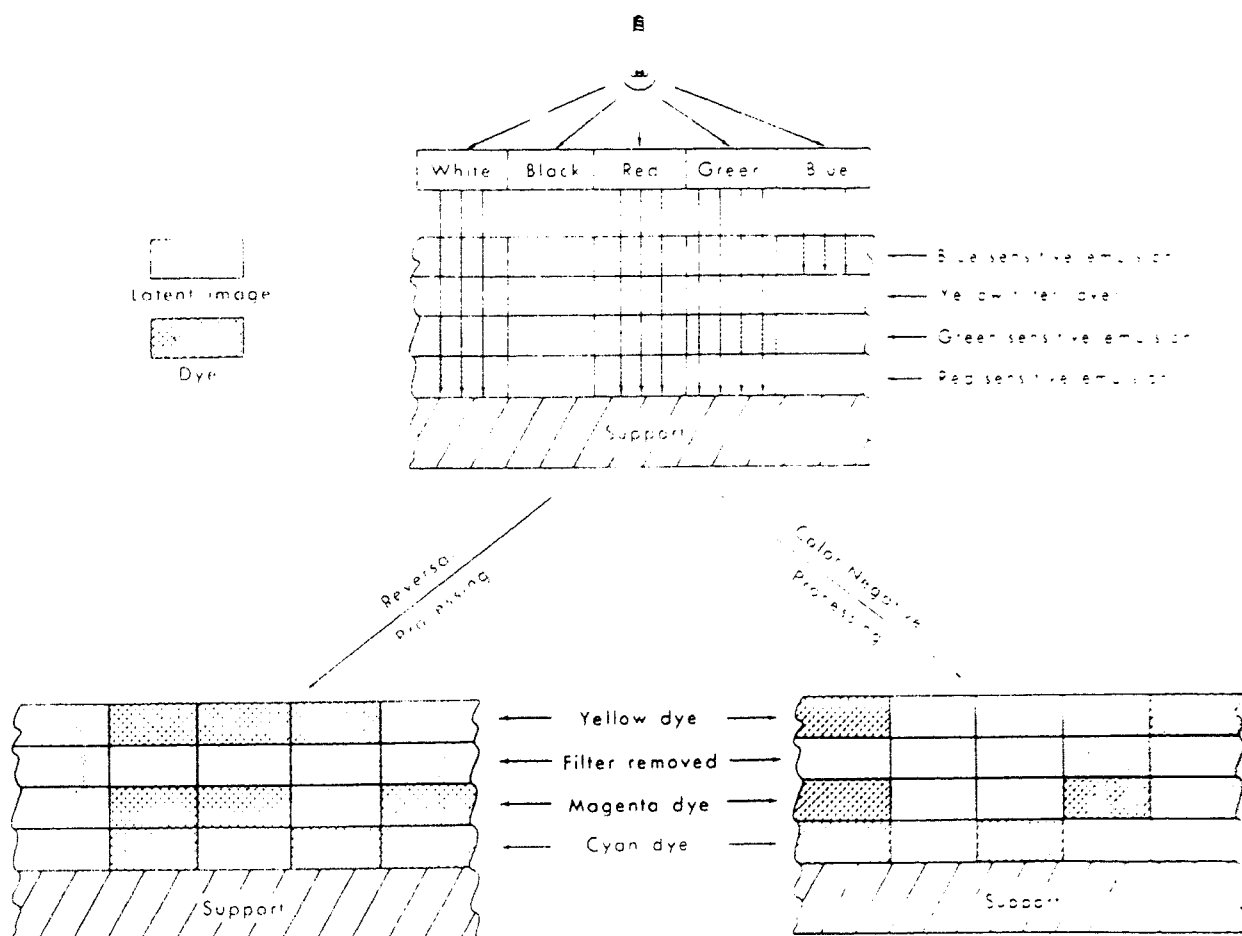
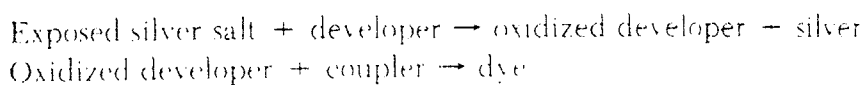
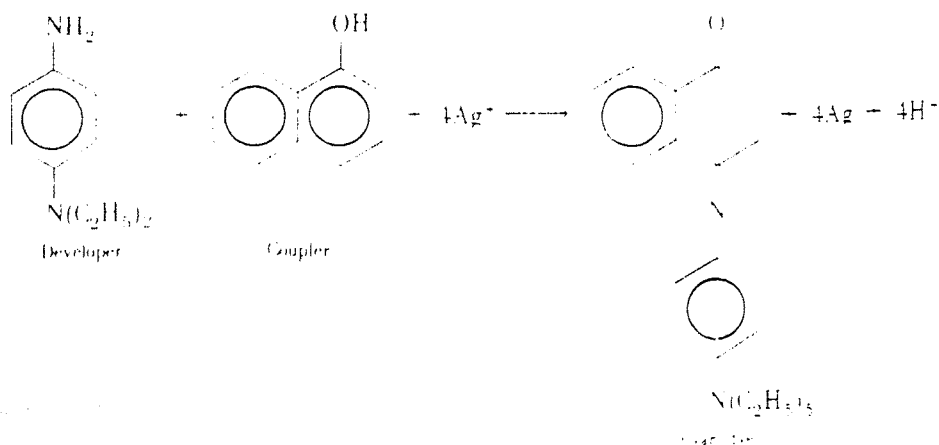


Fig. 7.1. Relation of dye images to the selective sensitivity of color photographic emulsions. (Fig. 7.1.2: Kodak Co.)

dye-forming reactions are:



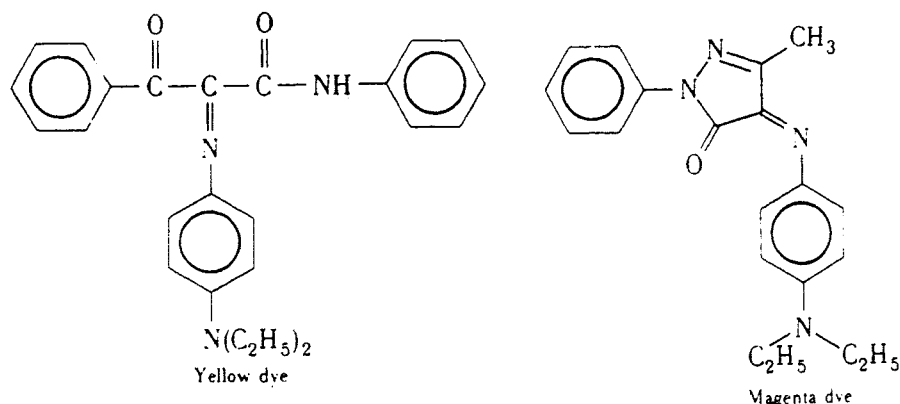
In the case of the specific developer, *N,N*-diethyl-*p*-phenylenediamine, and a specific coupler,  $\alpha$ -naphthol, the overall reaction can be written



The overall reaction is a redox reaction. The developer is oxidized to a quinonoid structure, and the silver ion is reduced to silver metal. The coupler is then oxidized to a quinonoid structure, which forms a dye with the oxidized developer.



This dye, of the indoaniline class, is cyan. From benzoylacetanilide as the coupler, a yellow dye of the azomethine type results, and from a pyrazolone, a magenta dye is formed:



Such dyes are of the Kodachrome type and involve inclusion of the coupler in the developer solution. *Such a process requires that only one layer develop at a time and that all reactants be washed out of the photographic material before the next dye is produced.* Careful control is needed to prepare each layer for development. If, however, the bulk of the coupler is increased so that it cannot diffuse through gelatin and certain other characteristics are introduced, the coupler can be incorporated in the emulsion by the manufacturer. The exposed silver salts can then be developed in all layers simultaneously. The oxidized developer finds the proper coupler in the immediate vicinity and therefore forms the proper dye in the amount required by the subject.

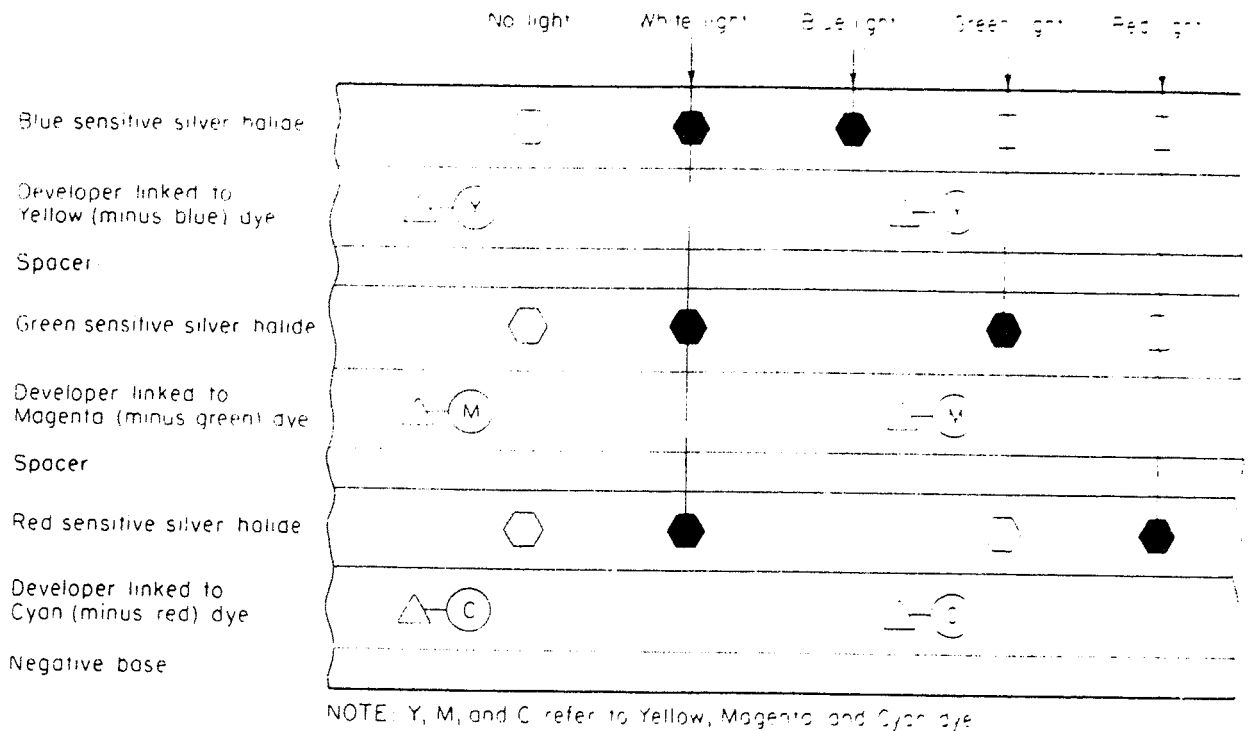
There are two major types of color photographic processing, negative and reversal, as indicated in Fig. 7.1. *Negative processing* involves incorporated couplers and results in color development in the region of the exposed silver salts. A color negative results in dyes complementary to the colors of the subject. Thus a yellow dye is formed in regions exposed to blue, a magenta dye in regions exposed to green, and a cyan dye in regions exposed to red. This negative can be used to make a positive print or any number of intermediate color pictures in order to introduce special effects, as in color cinematography. In making the print, the dyes in the negative control the amounts of blue, green, and red light reaching the color-sensitive emulsion layers on the print material. The latter emulsions, like those of the negative, contain incorporated couplers.

*Reversal processes* involve the development of exposed silver salts to a silver negative. The remaining silver salts are exposed selectively, and color developed to yield dye layer by layer, as in Kodak Kodachrome film, or are exposed or chemically fogged in toto and developed to yield dyes in all layers simultaneously, as in Kodak Ektachrome film, which contains incorporated couplers.

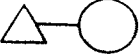
New processes of color photography are being introduced. One of these, *Polacolor* (Fig. 7.2), a product of the Polaroid Corp., depends upon incorporation in the light-sensitive layer of preformed dyes to which developing agents are chemically attached. The process is accomplished as described above by sensitized emulsion layers. The dye developers are soluble in the alkaline processing solution; however, as an image is developed, the dye developer is converted to an insoluble, immobile form. Dye-developer molecules not involved with image development diffuse from the emulsions and are mordanted on a receiver, which becomes the print.

Polaroid's SX-70 system<sup>6</sup> involves the exposure of the film and its almost immediate exit

<sup>6</sup>Fast Film, Powerful Battery Improves Polaroids, *Chem. Eng. News* 59 (25) 52 (1981); Land, One-Step Photography, *Photog. Sci. Eng.* 16 (4) 147 (1972).



**Fig. 7.2.** Development process of Polaroid-Land cameras. Structure of the negative: The principal layers of the negative are shown *magnified 6000 times*. The total thickness of all these layers coated on a sturdy base) is less than half the thickness of a human hair.

 This symbol represents an entirely new kind of molecule, which is a dye linked to a developer by an inactive atomic thread. This nonconducting leash does not allow interchange of electronic charges between the dye and developer, but it does give the developer group control over the movement of the dye. The dye part of these hitched molecules must be different in each layer.



These are unexposed grains of silver halide.

These are exposed grains of silver halide. Note, for example, how a ray of green light will pass through the blue-sensitive layer without exposing the silver halide and will expose a grain in the green layer, but not in the red layer.

In Polaroid cameras, where the exposure and development processes are carried on in the camera itself, the inventor Land uses a novel method of development for both black-and-white and color pictures, wherein the processing liquid is spread from "pods" in a thin viscous layer between the negative and the positive as the two are pressed together. Land developed the diffusion-transfer-reversal (DTR) process. This process produces a finished positive black-and-white or colored picture in a remarkably short time and directly from the camera. The Polaroid color film contains an entirely new kind of molecule developed for this use, namely, a dye (yellow, magenta, or cyan) in different layers linked to a developer by an inactive thread. Upon development (pod broken), the reagent reaches all parts of the extremely thin layers and, as it reaches a linked molecule of developer and dyer, it sets the linked molecules in motion.

When a linked molecule reaches a light-exposed silver grain, it becomes involved in the development of that grain and loses its mobility and acts to form its part in the image on the positive; e.g., a ray of green light exposes a silver halide in that layer and traps a linked molecule of developer and magenta dye. Likewise, this happens for other colors of light, building up the complementary color. All these unite together in their respective layers to form the color positive. (Polaroid Corp.)

from the camera into many million times as much light as is used to expose it. This was accomplished by synthesizing indicator dyes that have high absorption coefficients at high pH values and that become colorless at lower pH values. The exposed film passes through the rollers of the camera which force a small quantity of alkali and titanium dioxide between the layers. The dissolved dye developers diffuse upward through the emulsion layers. When an exposed silver halide grain is met, the developers are oxidized and immobilized within the emulsion. Molecules of dye developers that do not come into contact with exposed grains